(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 January 2003 (16.01.2003)

PCT

(10) International Publication Number
WO 03/004735 A1

(51) International Patent Classification⁷: D01D 5/00

(21) International Application Number: PCT/KR01/02158

(22) International Filing Date: 13 December 2001 (13.12.2001)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
2001-39789 4 July 2001 (04.07.2001) KR
2001/41854 12 July 2001 (12.07.2001) KR

(71) Applicant and
(72) Inventor: KIM, Hag-Yong [KR/KR]; 167-141, Dukjin-dong, Dukjin-gu, Chonju-city, 561-756 Chonrabuk-do (KR).

(74) Agent: CHO, Hwal-Rai; Suite No. 1507 Yoksam Heights Bldg, 642-19 Yoksam-dong, Kangnam-gu, 135-981 Seoul (KR).

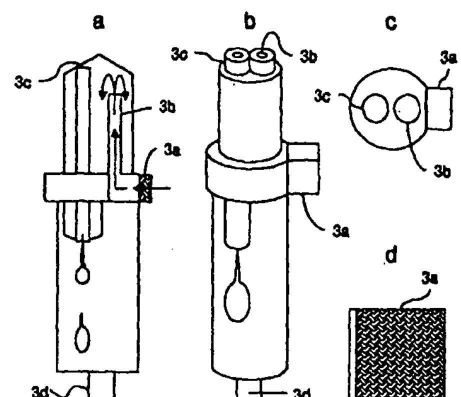
(81) Designated States *(national)*: CN, JP, US.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: AN ELECTRONIC SPINNING APPARATUS, AND A PROCESS OF PREPARING NONWOVEN FABRIC USING THE THEREOF



(57) Abstract: The present invention relates to an electrospinning apparatus including a spinning dope drop device (3) formed between a metering pump (2) and a nozzle block (4), the spinning dope drop device (3) including (i) a sealed cylindrical shape, (ii) a spinning dope inducing tube 3c and a gas inletting tube 3b receiving gas through its lower end and having its gas inletting part connected to a filter 3a being aligned side by side at the upper portion of the spinning dope drop device, (iii) a spinning dope discharge tube 3d being protruded from the lower portion of which, and (iv) a hollow unit for dropping the spinning dope from the spinning dope inducing tube 3c being formed at the middle portion of which. In addition, a method for preparing a non-woven fabric drops flowing of a spinning dope at least once by passing the spinning dope through a spinning dope drop device (3) before supplying the spinning dope to a nozzle block (4) supplied with a voltage in electrospinning. As a result, the present invention can mass-produce the nano fibers and non-woven fabrics by maximizing fiber formation effects in electrospinning, and easily control a width and thickness of the non-woven fabric.

WO 03/004735 A1

AN ELECTRONIC SPINNING APARATUS, AND A PROCESS OF PREPARING NONWOVEN FABRIC USING THE THEREOF

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an electronic spinning(electrospinning) apparatus for mass-producing nano fibers, and a process for preparing a non-woven fabric using the same.

Description of the Related Art

A conventional electrospinning apparatus and a process for preparing a non-woven fabric using the same have been disclosed under U.S. Patent No. 4,044,404. As shown in Figure 1, the conventional electrospinning apparatus of the patent '404 includes: a spinning dope main tank 1 for storing a spinning dope; a metering pump 2 for quantitatively supplying the spinning dope; a plurality of nozzles for discharging the spinning dope; a collector 6 positioned at the lower end of the nozzles, for collecting the spun fibers; a voltage generator 11 for generating a voltage; and a plurality of instruments for transmitting the voltage to the nozzles and the collector 6.

The conventional process for preparing the non-woven fabric using the electronic spinning apparatus will now be described in detail. The spinning dope of the spinning dope main tank 1 is consecutively quantitatively provided to the plurality of nozzles supplied with a high voltage through the metering pump 2.

Continuously, the spinning dope supplied to the nozzles is spun and collected on the collector 6 supplied with the high voltage through the nozzles, thereby forming a single fiber web.

Continuously, the single fiber web is embossed or needle-punched to prepare the non-woven fabric.

However, the conventional electrospinning apparatus and process for preparing the non-woven fabric using the same have a disadvantage in that an effect of electric force is reduced because the spinning dope is consecutively supplied to the nozzles having the high voltage.

In more detail, the electric force transmitted to the nozzles is dispersed to the whole spinning dope, and thus fails to overcome interface or surface tension of the spinning dopes. As a result, fiber formation effects by the electric force are deteriorated, which hardly achieves mass production of the fiber.

Moreover, the spinning dope is spun through the plurality of nozzles, not through nozzle blocks. It is thus difficult to control a width and thickness of the non-woven fabric.

SUMMARY OF THE INVENTION

It is therefore, an object of the present invention to provide an electronic spinning apparatus which can mass-produce nano fibers by enhancing fiber formation effects by maximizing an electric force supplied to a nozzle block in electronic spinning, namely maintaining the electric force higher than interface or surface tension of a spinning dope.

It is another object of the present invention to provide a process for easily controlling a width and thickness of a non-woven fabric by using an electrospinning apparatus having a nozzle block in which a plurality of pins are connected.

It is yet another object of the present invention to provide a process for preparing a non-woven fabric irregularly coated with nano fibers by using the electrospinning apparatus.

In order to achieve the above-described objects, there is provided an electrospinning apparatus comprising: a spinning dope drop device 3 positioned between the metering pump 2 and the nozzle block 6, and the spinning dope drop device including: (i) a sealed cylindrical shape, (ii) a spinning dope inducing tube 3c and a gas inletting tube 3b receiving gas through its lower end and having its gas inletting part connected to a filter 3a being aligned side by side at the upper portion of the spinning dope drop device, (iii) a spinning dope discharge tube 3d being protruded from the lower portion of which, and (iv) a hollow unit for dropping the spinning dope from the spinning dope inducing tube 3c being formed at the middle portion of which.

In addition, a method for preparing a non-woven fabric drops flowing of a spinning dope at least once by passing the spinning dope through a spinning dope drop device before supplying the spinning dope to a nozzle block supplied with a voltage in electronic spinning.

An electronic spinning apparatus, and a process for preparing a non-woven fabric using the same in accordance with preferred embodiments of the present invention will now be described in detail with reference to the

accompanying drawings.

Referring again to Figure 1, the electrospinning apparatus includes: a spinning dope main tank 1 for storing a spinning dope; a metering pump 2 for quantitatively supplying the spinning dope; a nozzle block 4 having block-type nozzles composed of a plurality of pins, and discharging the spinning dope in a fiber shape; a collector 6 positioned at the lower end of the nozzle block 4, for collecting spun single fibers; a voltage generator 11 for generating a high voltage; a voltage transmission rod 5 for transmitting the voltage generated in the voltage generator 11 to the upper end of the nozzle block 4; and a spinning dope drop device 3 positioned between the metering pump 2 and the nozzle block 4.

As illustrated in Figures 4a to 4d, the spinning dope drop device 3 has a sealed cylindrical shape. A spinning dope inducing tube 3c for inducing the spinning dope to the nozzle block and a gas inletting tube 3b are aligned side by side at the upper end of the spinning dope drop device 3. Here, the spinning dope inducing tube 3c is formed slightly longer than the gas inletting tube 3b.

The gas inlets from the lower end of the gas inletting tube 3b, and an initial gas inletting portion of the gas inletting tube 3b is connected to a filter 3a shown in Figure 4d. A spinning dope discharge tube 3d for inducing the dropped spinning dope to the nozzle block 4 is formed at the lower end of the spinning dope drop device 3. The center portion of the spinning dope drop device 3 is hollow so that the spinning dope can be dropped from the end of the spinning dope inducing tube 3c.

The spinning dope inputted to the spinning dope drop device 3 is flown

through the spinning dope inducing tube 3c, but dropped at the end thereof. Therefore, flowing of the spinning dope is intercepted at least one time.

The principle of dropping the spinning dope will now be explained in detail. When the gas inlets into the upper end of the spinning dope drop device 3 through the filter 3d and the gas inletting tube 3b, a pressure of the spinning dope inducing tube 3c becomes irregular due to gas eddy. Such a pressure difference drops the spinning dope.

An inert gas such as air or nitrogen can be used as the gas.

On the other hand, the nozzles are aligned in block units having at least two pins. One nozzle block 4 includes 2 to 100,000 pins, preferably 20 to 2,000 pins. The nozzle pins have circular or different shape sections. In addition, the nozzle pins can be formed in an injection needle shape. The nozzle pins are aligned in a circumference, grid or line, preferably in a line.

The process for preparing the non-woven fabric using the electro-spinning apparatus in accordance with the present invention will now be described.

Firstly, a thermoplastic or thermosetting resin spinning dope stored in the main tank 1 is measured by the metering pump 2, and quantitatively supplied to the spinning dope drop device 3. Exemplary thermoplastic or thermosetting resins used to prepare the spinning dope include polyester resins, acryl resins, phenol resins, epoxy resins, nylon resins, poly(glycolide / L-lactide) copolymers, poly(L-lactide) resins, polyvinyl alcohol resins and polyvinyl chloride resins. A resin molten solution or resin solution may be used as the spinning dope.

When the spinning dope supplied to the spinning dope drop device 3 passes through the spinning dope drop device 3, flowing of the spinning dope is dropped at least once in the mechanism described above. Thereafter, the spinning dope is supplied to the nozzle block 4 having a high voltage.

The nozzle block 4 discharges the spinning dope in a single fiber shape through the nozzles. The spinning dope is collected by the collector 6 supplied with the high voltage to prepare a non-woven fabric web.

Here, to facilitate fiber formation by the electric force, a voltage over 1kV, more preferably 20kV is generated in the voltage generator 11 and transmitted to the voltage transmission rod 5 and the collector 6 installed at the upper end of the nozzle block 4. It is advantageous in productivity to use an endless belt as the collector 6.

The non-woven fabric web formed on the collector 6 is consecutively processed by an embossing roller 9, and the prepared non-woven fabric winds on a winding roller 10. Thus, the preparation of the non-woven fabric is finished.

In another aspect of the present invention, as shown in Figure 2 and Figure 3, nano fibers are elctrospun on one surface or both surfaces of a fiber material by using the electrospinning apparatus, and bonded. Exemplary fiber materials include fiber products such as spun yarns, filaments, textiles, knitted fabrics and non-woven fabrics, paper, films and braids.

Before spinning the nano fibers on the fiber material, the fiber material can be dipped in an adhesive solution and compressed by a compression roller 15. When the fiber material is dipped in the adhesive solution and compressed, the fiber material is preferably dried by a drier 16 before being bonded by a

bonding device 17.

The fiber material on which the nano fibers are spun and adhered can be bonded according to needle punching, compression by a heating embossing roller, high pressure water injection, electromagnetic wave, ultrasonic wave or plasma.

As depicted in Figure 3, when at least two electrospinning apparatuses are employed, the spinning dopes supplied to the respective electrospinning apparatuses include different kinds of polymers. Here, the nano fibers can be coated in a hybrid type.

Still referring to Figures 2 and 3, the electrospinning apparatus includes: a spinning dope main tank 1 for storing a spinning dope; a metering pump 2 for quantitatively supplying the spinning dope; a nozzle block 4 having block-type nozzles composed of a plurality of pins, and discharging the spinning dope onto fibers; a voltage transmission rod 5 positioned at the lower end of the nozzle block 4; a voltage generator 11 for generating a high voltage; and a spinning dope drop device 3 positioned between the metering pump 2 and the nozzle block 4.

The spinning dope drop device 3 was mentioned above.

The electronspinning process to make the nano fibers by using the electrospinning apparatus of the present invention will now be explained in more detail.

Firstly, a thermoplastic or thermosetting resin spinning dope stored in the main tank 1 is measured by the metering pump 2, and quantitatively supplied to the spinning dope drop device 3. Exemplary thermoplastic or

thermosetting resins used to prepare the spinning dope include polyester resins, acryl resins, phenol resins, epoxy resins, nylon resins, poly(glycolide / L-lactide) copolymers, poly(L-lactide) resins, polyvinyl alcohol resins and polyvinyl chloride resins. A resin molten solution or resin solution may be used as the spinning dope.

Supplied to the spinning dope drop device 3, the spinning dope passes through it, flowing of the spinning dope is dropped at least once in the mechanism described above. Thereafter, the spinning dope is supplied to the nozzle block 4 having a high voltage.

Then the nozzle block 4 discharges the spinning dope to the fiber material in a single fiber shape through the nozzles.

Here, to facilitate fiber formation by the electric force, a voltage over 1kV, more preferably 20kV is generated in the voltage generator 11 and transmitted to the upper end of the nozzle block 4 and the voltage transmission rod 5.

In accordance with the present invention, when the spinning dope is supplied to the nozzle block 4, flowing of the spinning dope is dropped at least once by using the spinning dope drop device 3, thereby maximizing fiber formation. As a result, fiber formation effects by the electric force are improved to mass-produce the nano fibers and non-woven fabrics. Moreover, since the nozzles having the plurality of pins are aligned in block units, a width and thickness of the non-woven fabric can be easily controlled.

When at least two electrospinning apparatuses are aligned, polymers having a variety of components can be combined one another, which makes it easier to prepare a hybrid non-woven fabric.

In accordance with the present invention, a diameter of the fiber spun by melting spinning is over 1,000nm, and a diameter of the fiber spun by solution spinning ranges from 1 to 500nm. The solution spinning includes wet spinning and dry spinning.

The non-woven fabric composed of the nano fibers is used as medical materials such as an artificial organisms, hygienic band, filter, synthetic blood vessel, and as industrial materials which is semiconductor wipers and battery.

For examples, a mask coated with the nano fibers is useful as an anti-bacteria mask, and a spun yarn or filament coated with the nano fibers is useful as a yarn for artificial suede and leather. In addition, coating nylon 6 nano fibers on a paper filter extends a life span of the filter. The fiber material coated with the nano fibers is soft to the touch.

BRIEF DESCRIPTION OF THE DRAWINGS

The above objects, features and advantages of the present invention will become more apparent from the following preferred embodiments when taken in conjunction with the accompanying drawings, in which:

Figure 1 is a schematic view illustrating an electrospinning apparatus in accordance with the present invention;

Figure 2 is a schematic view illustrating a process of consecutively coating first component nano fibers in accordance with the present invention;

Figure 3 is a schematic view illustrating a process of consecutively coating second component nano fibers in accordance with the present

invention;

Figure 4a is a cross-sectional view illustrating a spinning dope drop device 3;

Figure 4b is a perspective view illustrating the spinning dope drop device 3;

Figure 4c is a plan view illustrating the spinning dope drop device 3;

Figure 4d is an enlarged view illustrating a filter of the spinning dope drop device 3;

Figure 5 is a schematic view illustrating a process of assembling two electronic spinning apparatuses in accordance with the present invention;

Figure 6 is SEM(scanning electron microscope) shown a non-woven fabric prepared by using nylon 6 spinning dope dissolved in formic acid in accordance with the process of the present invention;

Figure 7 is SEM to magnify Figure 4;

Figure 8 is SEM shown a non-woven fabric prepared with poly(L-lactide) spinning dope dissolved in methylene chloride in accordance with the process of the present invention;

Figure 9 is a diameter distribution of nano fibers elctropsun poly(glycolide-lactide) copolymer spinning dope by using electrospinning in accordance with the process of the present invention;

Figure 10 is SEM shown a non-woven fabric prepared with polyvinyl alcohol spinning dope dissolved in distilled water in accordance with the process of the present invention;

Figure 11 is SEM to magnify Figure 10;

Figure 12 is SEM shown a non-woven fabric electrospun with a nozzle width of 90cm;

Figure 13 is SEM shown a paper filter (product of Example 5) coated with polyvinyl alcohol nano fibers;

Figure 14 is thermogravimetric analysis curves shown polyvinyl alcohol nano fibers themselves as a function of curing time;

Figure 15 is differential scanning calorimeter(DSC) curves shown polyvinyl alcohol nano fibers themselves as a function of curing time;

Figure 16 is SEM of polyester fabric (product of Example 6) coated with nylon 6 nano fibers;

Figure 17 is SEM of nylon 6 fabric (product of Example 7) coated with nylon 6 nano fibers;

Figure 18 is SEM of polyester filament (product of Example 8) coated with nylon 6 nano fibers; and

Figure 19 is SEM of nylon 6 non-woven fabrics coated with polyurethane polymers.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Hereinafter, the present invention will be described in more detail through examples, but it is not limited thereto.

Example 1

Nylon 6 chip having relative viscosity of 2.3 was dissolved in formic acid by 20% in 96% of sulfuric acid solution, to prepare a spinning dope. The

spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 2, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning dope was supplied to the nozzle block 4 having a voltage of 50kV, and spun in a fiber shape through the nozzles. The spun fibers were collected on the collector 6, to prepare a non-woven fabric web having a width of 60cm and weight of 3.0g/m^2. Here, each nozzle block included 200 pins, and 200 nozzle blocks were aligned. Model CH 50 of Symco Corporation was used as the voltage generator. The output rate per one pin was 0.0027g/min (discharge amount of one nozzle block : 0.54g/min), and thus a throughput was 108g/min. One nozzle block was divided into 10, and one spinning dope drop device 3 was installed in every 20 pins. A drop speed had 3-second intervals. The non-woven fabric web was transferred and embossed at a speed of 60m/min, to prepare a non-woven fabric. Table 1 shows tensile strength and tensile elongation at break. Figure 6 and Figure 7 are illustrated SEM of the prepared nylon 6 non-woven fabric.

Example 2

Poly(L-lactide) having a viscosity average molecular weight of 450,000 was dissolved in methylene chloride, to prepare a spinning dope. The spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 2, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning dope was supplied to the nozzle block 4 having a voltage of 50kV, and spun in a fiber shape through the nozzles. The spun fibers were collected on the collector

6, to prepare a non-woven fabric web having a width of 60cm and weight of 6.9g/m^2. Here, each nozzle block included 400 pins, and 20 nozzle blocks were aligned. Model CH 50 of Symco Corporation was used as the voltage generator. The output rate per one pin was 0.0026g/min, and thus a throughput was 20.8g/min. One nozzle block was divided into 10, and one spinning dope drop device 3 was installed in every 40 pins. A drop speed had 3.2-second intervals. The non-woven fabric web was transferred and embossed at a speed of 5m/min, to prepare a non-woven fabric. Table 1 shows tensile strength and tensile elongation at break. SEM of the prepared poly(L-lactide) non-woven fabric was shown in Figure 8.

Example 3

Poly(glycolide-lactide) copolymer (mole ratio : 50/50) having a viscosity average molecular weight of 450,000 was dissolved in methylene chloride, to prepare a spinning dope. The spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 2, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning dope was supplied to the nozzle block 4 having a voltage of 50kV, and spun in a fiber shape through the nozzles. The spun fibers were collected on the collector 6, to prepare a non-woven fabric web having a width of 60cm and weight of 8.53g/m^2. Here, each nozzle block included 400 pins, and 20 nozzle blocks were aligned. Model CH50 of Symco Corporation was used as the voltage generator. The throughput per one pin was 0.0032g/min (output rate per one nozzle block : 1.28g/min), and thus a total output rate was 25.6g/min. One nozzle block was divided into 10, and one

spinning dope drop device 3 was installed in every 40 pins. A drop speed had 2 second intervals. The non-woven fabric web was transferred and embossed at a speed of 5m/min, to prepare a non-woven fabric. Table 1 shows tensile strength and tensile elongation at break. Figure 9 shows the fiber diameter distribution of the prepared non-woven fabric.

Example 4

Polyvinyl alcohol having a number average molecular weight of 20,000 was dissolved in distilled water, to prepare a spinning dope. The spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 2, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning dope was supplied to the nozzle block 4 having a voltage of 50kV, and spun in a fiber shape through the nozzles. The spun fibers were collected on the collector 6, to prepare a non-woven fabric web having a width of 60cm and weight of 3.87g/m^2. Here, each nozzle block included 400 pins, and 20 nozzle blocks were aligned. Model CH 50 of Symco Corporation was used as the voltage generator. The output per one pin was 0.0029g/min (output rate per one block: 1.28g/min), and thus a total throughput was 23.2g/min. One nozzle block was divided into 10, and one spinning dope drop device 3 was installed in every 40 pins. A drop speed had 2.5-second intervals. The non-woven fabric web was transferred and embossed at a speed of 10m/min, to prepare a non-woven fabric. Table 1 shows tensile strength and tensile elongation at break. Figure 10 shows SEM of the prepared poly(vinyl alcohol) non-woven fabric.

<Table 1>

Tensile properties

Classification	Tensile Strength (kg/cm)	Tensile elongation at break(%)
Example 1	180	25
Example 2	180	25
Example 3	100	28
Example 4	120	32

* The tensile strength and tensile elongation were measured by ASTM D 1117.

Example 5

100wt% of polyvinyl alcohol having a number average molecular weight of 20,000, 2wt% of glyoxal and 1.8wt% of phosphoric acid were dissolved in distilled water, to prepare 15% of spinning dope. The spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 4, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning dope was supplied to the nozzle block 4 having a voltage of 45kV, and fibers having an average diameter of 105nm were continuously spun on the paper filter (width: 1m) transferred at a speed of 20m/min through the nozzles. The fibers were compressed (bonded) by the embossing roller, to prepare a coating web having a weight of 0.61g/m^2. Here, each nozzle block included 250 pins, and 20 nozzle blocks were aligned. Model name CH 50 of Symco Corporation was used as the voltage generator. The output per one pin was 0.0027g/min, and thus a total throughput was 13.5g/min. One nozzle block was divided into 10, and one spinning dope drop device 3 was installed in every 10 pins. A drop speed had 2.5-second intervals. The pins were formed in a circular shape. Figure 10 was shown the polyvinyl alcohol nano fibers themselves. SEM of Figure 10

magnified was shown in Figure 11. Figure 12 was the photographs to show the evidence the mass-production by using muti-pins and poly(vinyl alcohol). SEM of paper pulp coated with polyvinyl alcohol was illustrated in Figure 13. Figure 14 was shown the thermogravimetric analysis of poly(vinyl alcohol) nano fibers themselves with changing the curing time. Also, differential scanning calorimeter curves of nano fibers themselves as a function of the curing time were shown in Figure 15. When the coating paper pulp was processed in the drier of 160°C for 3 minutes and precipitated in toluene in a normal temperature for a day, it was not dissolved.

Example 6

Nylon 6 chip having a relative viscosity of 2.3 was dissolved in formic acid by 25% in 96% of sulfuric acid solution, to prepare a spinning dope. The spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 4, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning dope was supplied to the nozzle block 4 having a voltage of 45kV, and fibers having an average diameter of 108nm were continuously spun on polyester plane fabrics (width: 1m) passed through dipping and compression processes in acryl resin adhesive solution and transferred at a speed of 10m/min through the nozzles. The fibers were bonded (needle-punched) to prepare a coating web having a weight of 1.2g/m^2. Here, each nozzle block included 250 pins, and 20 nozzle blocks were aligned. Model CH 50 of Symco Corporation was used as the voltage generator. The throughput per one pin was 0.0024g/min, and thus a total output rate was 12.1g/min. One nozzle block was

divided into 10, and one spinning dope-drop device 3 was installed in every 10 pins. A drop speed had 3-second intervals. The pins were formed in a circular shape. SEM of the prepared coating polyester plane fabric was shown in Figure 16.

Example 7

Nylon 6 chip having a relative viscosity of 2.3 was dissolved in formic acid by 25% in 96% of sulfuric acid solution, to prepare a spinning dope. The spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 4, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning dope was supplied to the nozzle block 4 having a voltage of 45kV, and fibers having an average diameter of 108nm were continuously spun on nylon 6 plane fabric (width: 1m) passed through dipping and compression processes in acryl resin adhesive solution and transferred at a speed of 10m/min through the nozzles. The fibers were bonded (needle-punched) to prepare a coating web having a weight of 1.2g/m^2. Here, each nozzle block included 250 pins, and 20 nozzle blocks were aligned. Model CH 50 of Symco Corporation was used as the voltage generator. The output rate per one pin was 0.0024g/min, and thus a total throughput was 12.1g/min. One nozzle block was divided into 10, and one spinning dope drop device 3 was installed in every 10 pins. A drop speed had 3-second intervals. The pins were formed in a circular shape. SEM of the nylon 6 plane fabric coated was shown in Figure 17.

Example 8

Nylon 6 chip having a relative viscosity of 2.3 was dissolved in formic

acid by 25% in 96% of sulfuric acid solution, to prepare a spinning dope. The spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 3, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning dope was supplied to the nozzle block 4 having a voltage of 45kV, and fibers having an average diameter of 108nm were continuously spun and dried on 75 denier 36 filament polyester filament (alignment of 80 strips in 1 inch, width: 1m) passed through dipping and compression processes in acryl resin adhesive solution and transferred at a speed of 3m/min through the nozzles. Here, each nozzle block included 250 pins, and 20 nozzle blocks were aligned. Model CH 50 of Symco Corporation was used as the voltage generator. The output rate a one pin was 0.0024g/min, and thus a total throughput was 12.1g/min. One nozzle block was divided into 10, and one spinning dope drop device 3 was installed in every 10 pins. A drop speed had 3-second intervals. The pins were formed in a circular shape. A plane fabric(density: 80 threads/inch) was prepared by using the coating polyester filaments as warps and wefts. SEM of the polyester fabric coated was shown in Figure 18.

Example 9

Poly(glycolide-lactide) copolymer (mole ratio : 50/50) having a viscosity average molecular weight of 450,000 was dissolved in methylene chloride in a normal temperature, to prepare a spinning dope (density: 15%). The spinning dope was stored in the main tank 1, quantitatively measured by the metering pump 2, and supplied to the spinning dope drop device 3 of Figure 4, thereby discontinuously changing flowing of the spinning dope. Thereafter, the spinning

dope was supplied to the nozzle block 4 having a voltage of 48kV, and fibers having an average diameter of 108nm were continuously spun on poly(L-lactide) membrane film (weight : $10g/m^2$, width: 60cm) transferred at a speed of 2m/min through the nozzles. The fibers were bonded (needle-punched) to prepare a non-woven fabric web having a weight of $2.8g/m^2$. Here, each nozzle block included 200 pins, and 10 nozzle blocks were aligned. Model CH 50 of Symco Corporation was used as the voltage generator. The output rate per one pin was 0.0028g/min, and thus a total throughput was 5.6g/min. One nozzle block was divided into 10, and one spinning dope drop device 3 was installed in every 50 pins. A drop speed had 3-second intervals. The pins were formed in a circular shape. SEM of the non-woven fabric coated was shown in Figure 19.

INDUSTRIAL APPLICABILITY

The present invention mass-produces the non-woven fabric composed of the nano fibers, and easily controls the thickness and width of the non-woven fabric. In addition, when at least two electrospinning apparatuses are assembled, multi-component polymers can be easily combined, to prepare the hybrid non-woven fabric. Moreover, the non-woven fabric (fiber material) is coated with the nano fibers, and thus has improved softness and performance.

WHAT IS CLIMED IS:

1. An electrospinning apparatus constructed by a spinning dope main tank 1, a metering pump 2, a nozzle block 4, a collector 6 positioned at the lower end of the nozzle block, for collecting spun fibers, a voltage generator 11, a plurality of units for transmitting a voltage generated in the voltage generator to the nozzle block 4 and the collector 6, wherein the electrospinning apparatus is characterized in that comprising:

a spinning dope drop device 3 positioned between the metering pump 2 and the nozzle block 6, and the spinning dope drop device including:

(i) a sealed cylindrical shape,

(ii) a spinning dope inducing tube 3c and a gas inletting tube 3b receiving gas through its lower end and having its gas inletting part connected to a filter 3a being aligned side by side at the upper portion of the spinning dope drop device,

(iii) a spinning dope discharge tube 3d being protruded from the lower portion of which, and

(iv) a hollow unit for dropping the spinning dope from the spinning dope inducing tube 3c being formed at the middle portion of which.

0000

2. The apparatus according to claim 1, wherein the nozzles are aligned in block units having at least two pins or injection needles.

3. The apparatus according to claim 1 or 2, wherein a number of pins of one nozzle block ranges from 2 to 100,000.

4. The apparatus according to claim 1 or 2, wherein the nozzle pins have circular or different shape sections.

5. The apparatus according to claim 1 or 2, wherein the nozzle pins are aligned in a circumference shape, lattice shape or a row line.

6. A method for preparation of a non-woven fabric by electrospinning a thermoplastic or thermosetting resin spinning dope on a collector 6 from a nozzle block 4 and consecutively embossing a spun web, wherein the method is characterized in that comprising the step of:

passing a spinning dope from a spinning dope main tank 1 through a metering pump 2 and a spinning dope drop device 3 each other before supplying the spinning dope quantitatively supplied to the nozzle block 4 supplied with a voltage, and the spinning dope drop device 3 including:

(i) a sealed cylindrical shape,

(ii) a spinning dope inducing tube 3c and a gas inletting tube 3b receiving gas through its lower end and having its gas inletting part connected to a filter 3a being aligned side by side at the upper portion of the spinning dope drop device,

(iii) a spinning dope discharge tube 3d being protruded from the lower portion of which, and

(iv) a hollow unit for dropping the spinning dope from the spinning dope inducing tube 3c being formed at the middle portion of which.

7. The method according to claim 6, wherein the nozzles are aligned in block units having at least two pins.

8. The method according to claim 6, wherein air or inert gas inlets into the spinning dope drop device.

9. The method according to claim 6, wherein the spinning dope is melts or solution.

10. The method according to claim 6, wherein an endless belt is used as the collector 6.

11. A method for preparing a non-woven fabric coated with nano fibers comprising the steps of: spinning the nano fibers on one surface or both surfaces of a transferred fiber material by one or more electrospinning apparatuses including a spinning dope drop device 3, and bonding the nano fibers, wherein the spinning dope drop device 3 formed between a metering pump and a nozzle block includes: (i) a sealed cylindrical shape, (ii) a spinning dope inducing tube 3c and a gas inletting tube 3b receiving gas through its lower end and having its gas inletting part connected to a filter 3a being aligned side by side at the upper portion of the spinning dope drop device, (iii) a

spinning dope discharge tube 3d being protruded from the lower portion of which, and (iv) a hollow unit for dropping the spinning dope from the spinning dope inducing tube 3c being formed at the middle portion of which.

12. The method according to claim 11, wherein the fiber material is a spun yarn, filament, textile, knitted fabrics, non-woven fabric, paper, film or braid.

13. The method according to claim 11, wherein the fiber material is dipped and compressed in an adhesive solution before spinning nano fibers, and dried prior to bonding after spinning the nano fibers.

14. The method according to claim 11, wherein the bonding treatment is needle punching, thermal compression, electromagnetic wave treatment, high pressure water injection, supersonic wave treatment or plasma treatment.

15. The method according to claim 11, wherein spinning dopes supplied to the respective electronic spinning apparatuses have different polymers in case of using at least two electrospinning apparatuses.

16. The method according to claim 11, wherein the nozzles of the electrospinning apparatus are aligned in block units having at least two pins.

17. The method according to claim 11, wherein the number of pins of one nozzle block ranges from 2 to 100,000.

18. The method according to claim 11, wherein the nozzle pins have circular, injection needle type or different shape sections.

19. The method according to claim 11, wherein the nozzle pins are aligned in a circumference, grid or line.

20. The method according to claim 11, wherein air or inert gas inlets into the spinning dope drop device.

21. The method according to claim 11, wherein the spinning dope is melts or solution.

DRAWING

Fig 1

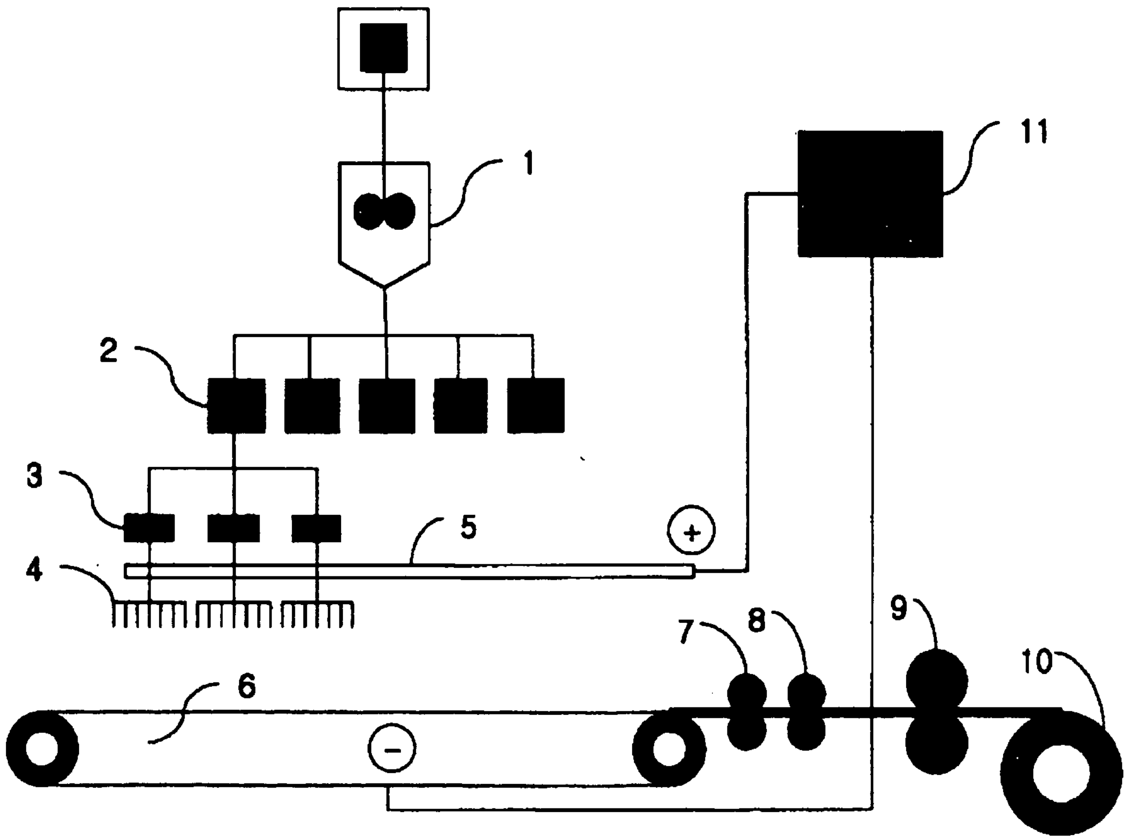


Fig 2

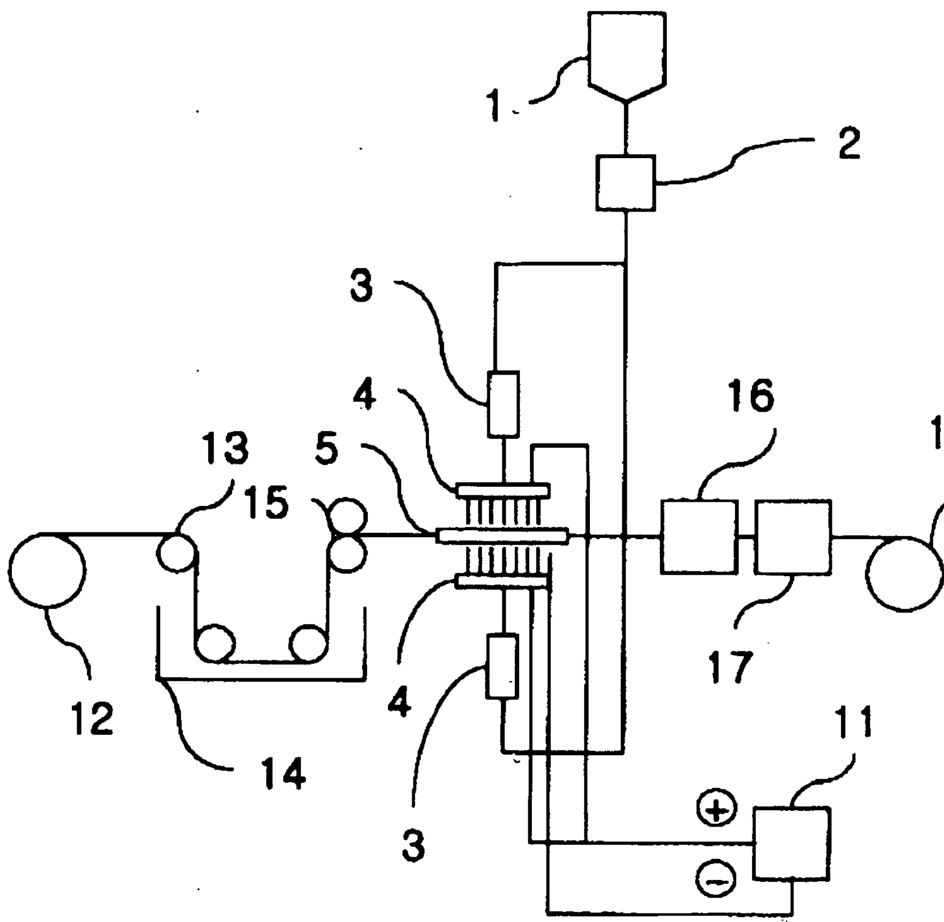


Fig 3

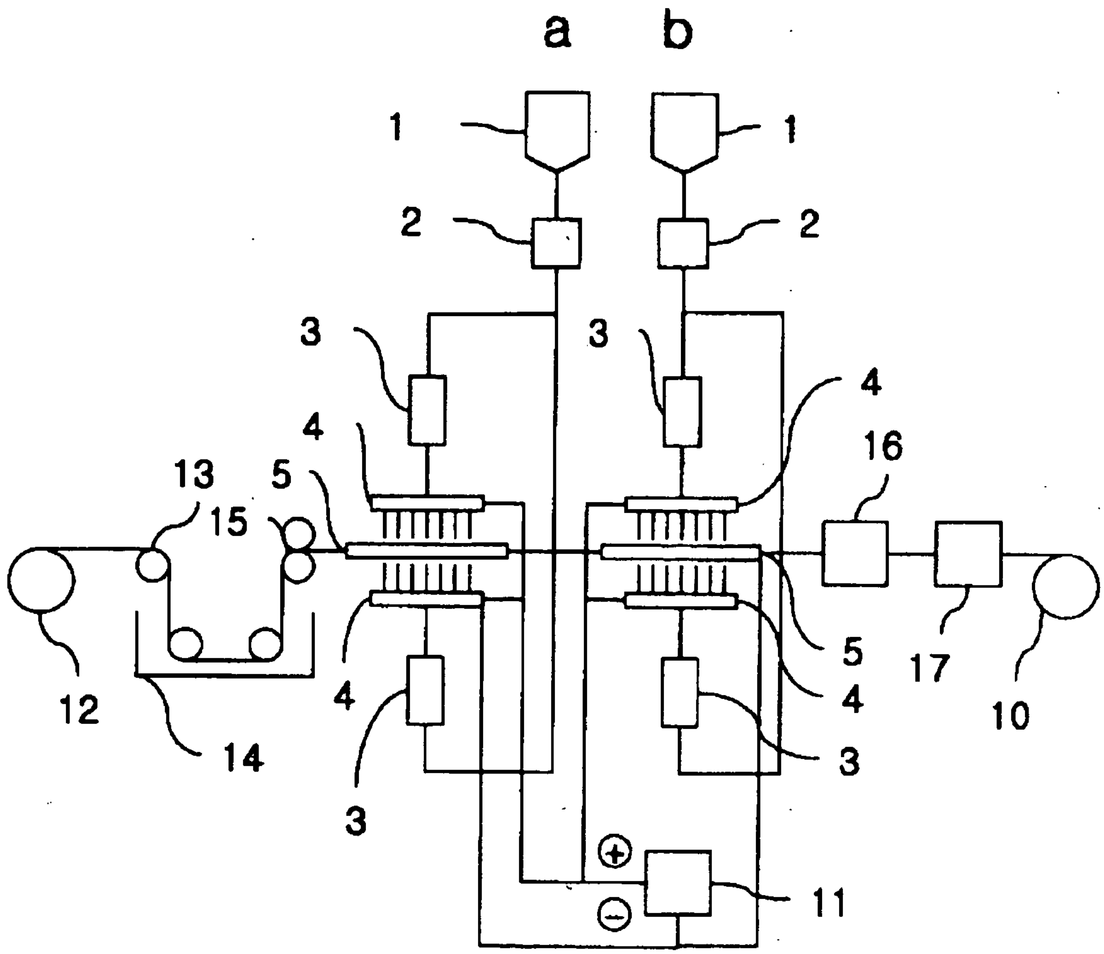


Fig 4

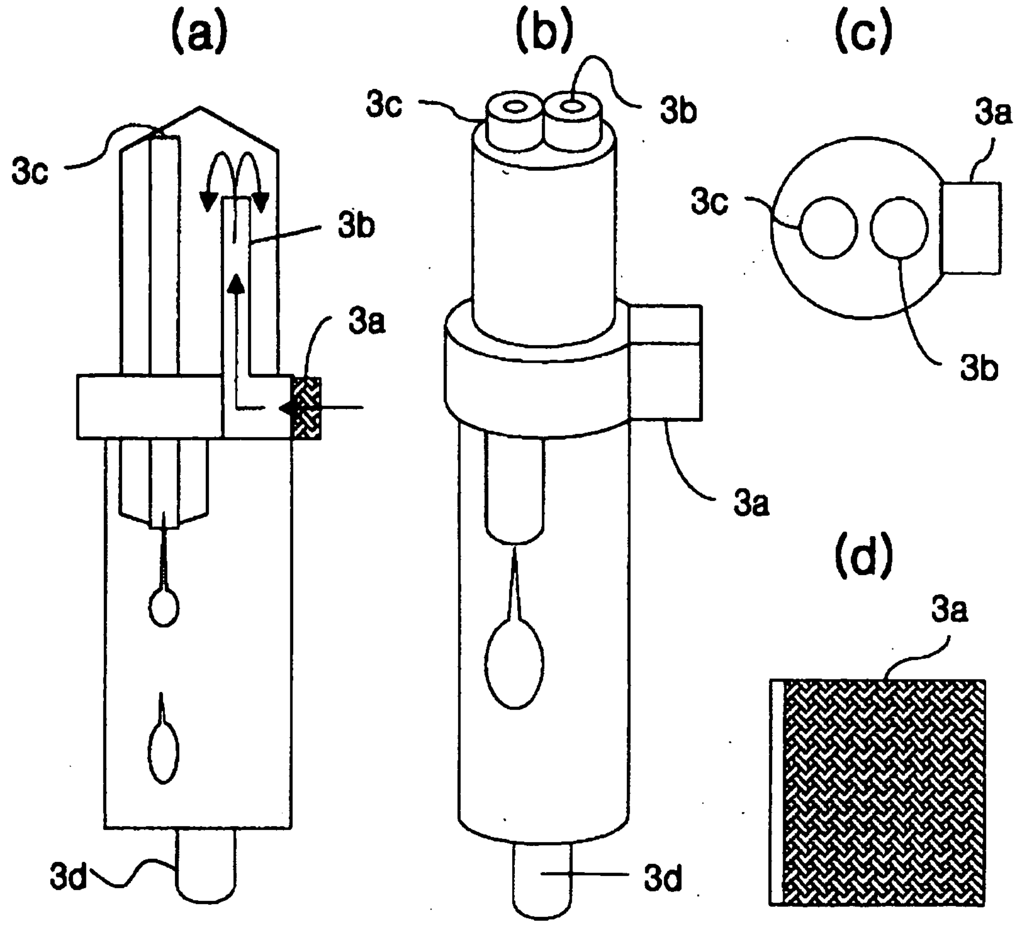


Fig 5

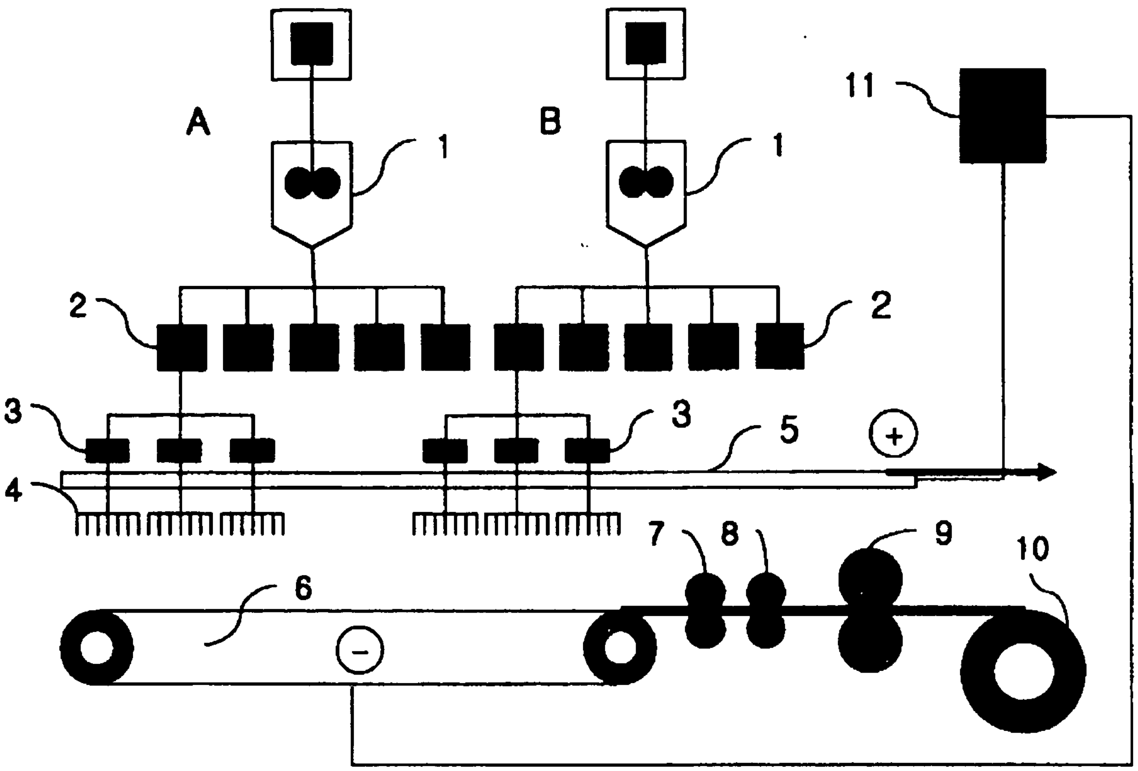


Fig 6

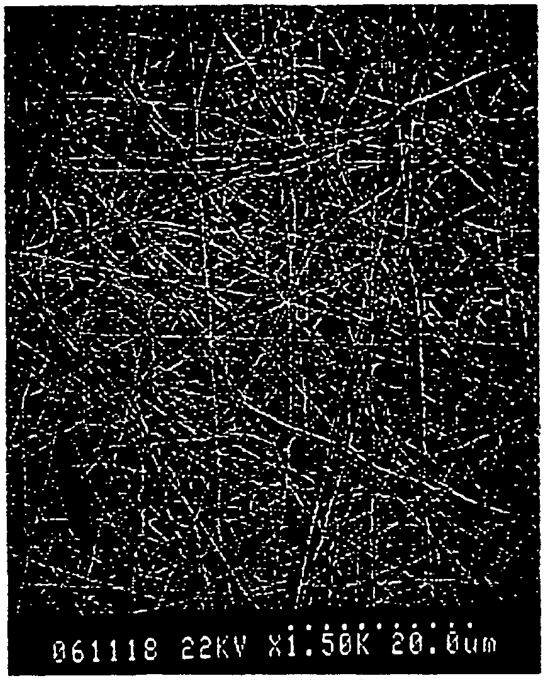


Fig 7

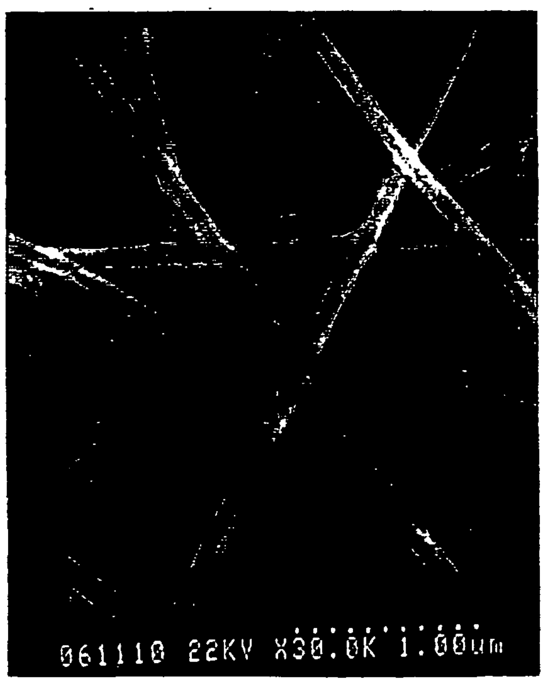


Fig 8

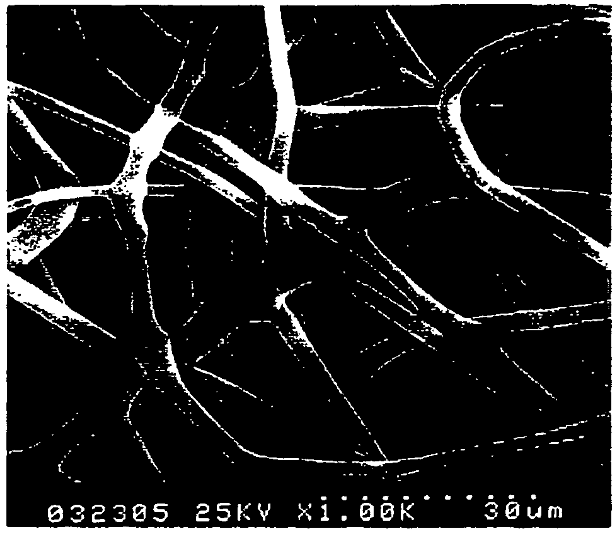


Fig 9

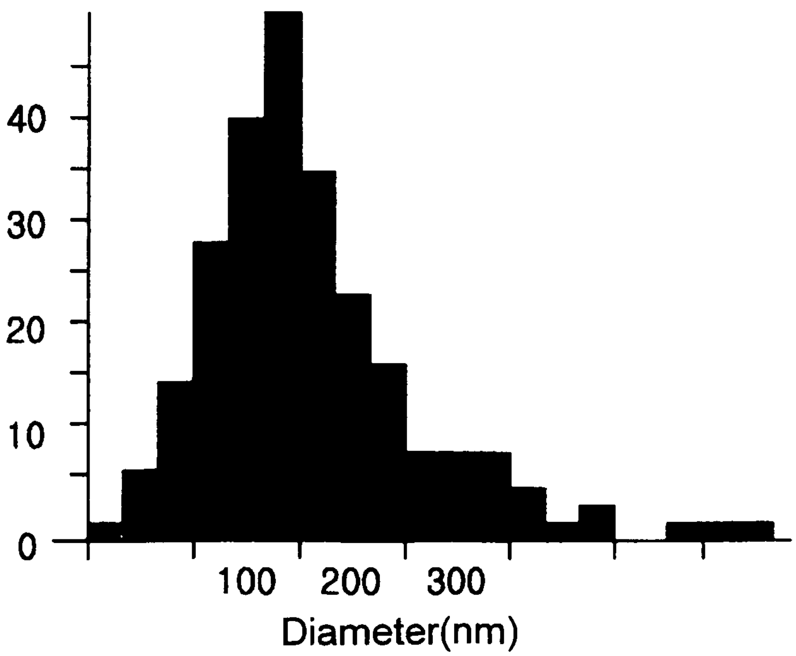


Fig 10

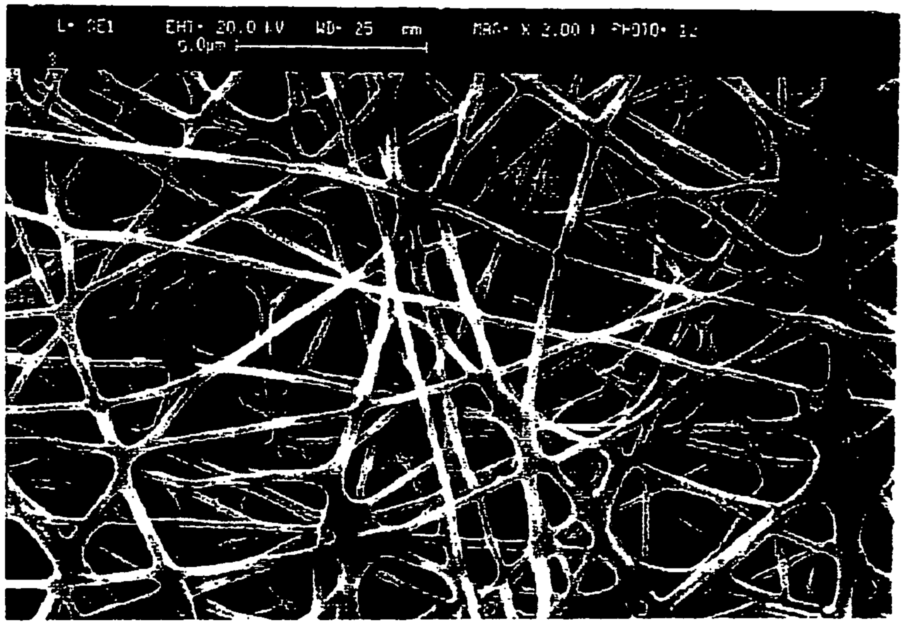


Fig 11

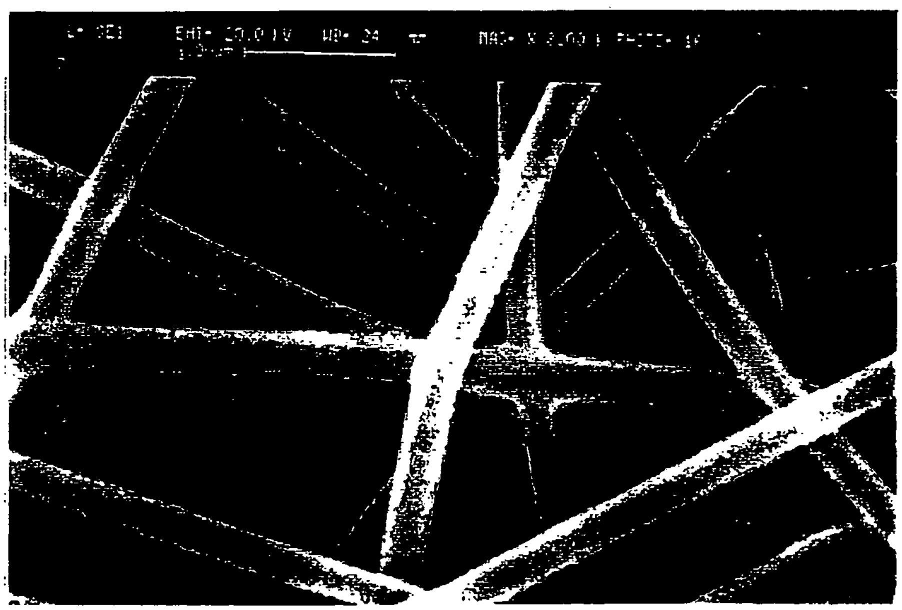


Fig 12

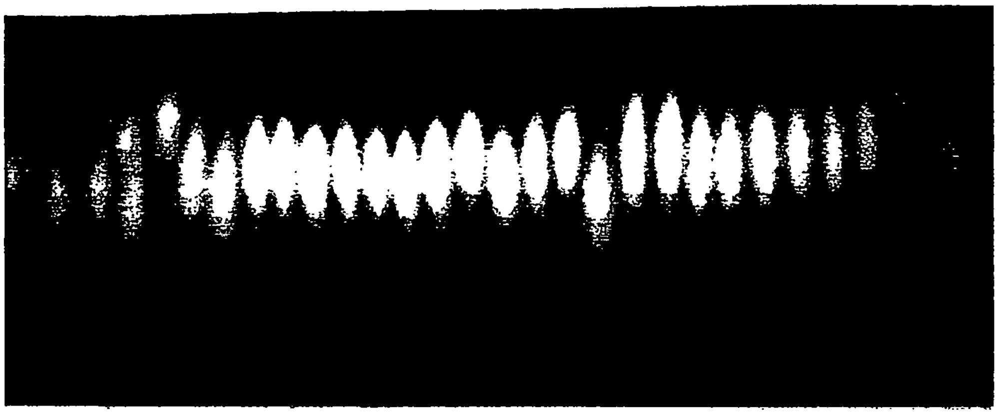


Fig 13

Fig 14

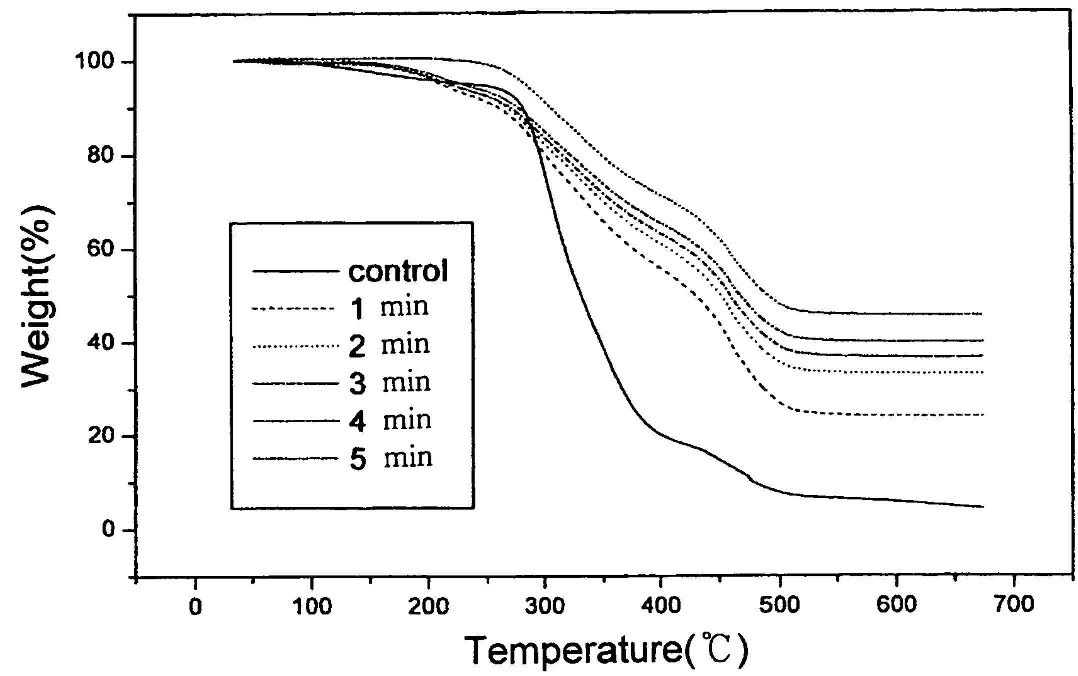

Weight(%)
100
80
60
40
20
0
0
100
200
300
400
500
600
700
Temperature(℃)
control
1 min
2 min
3 min
4 min
5 min

Fig 15

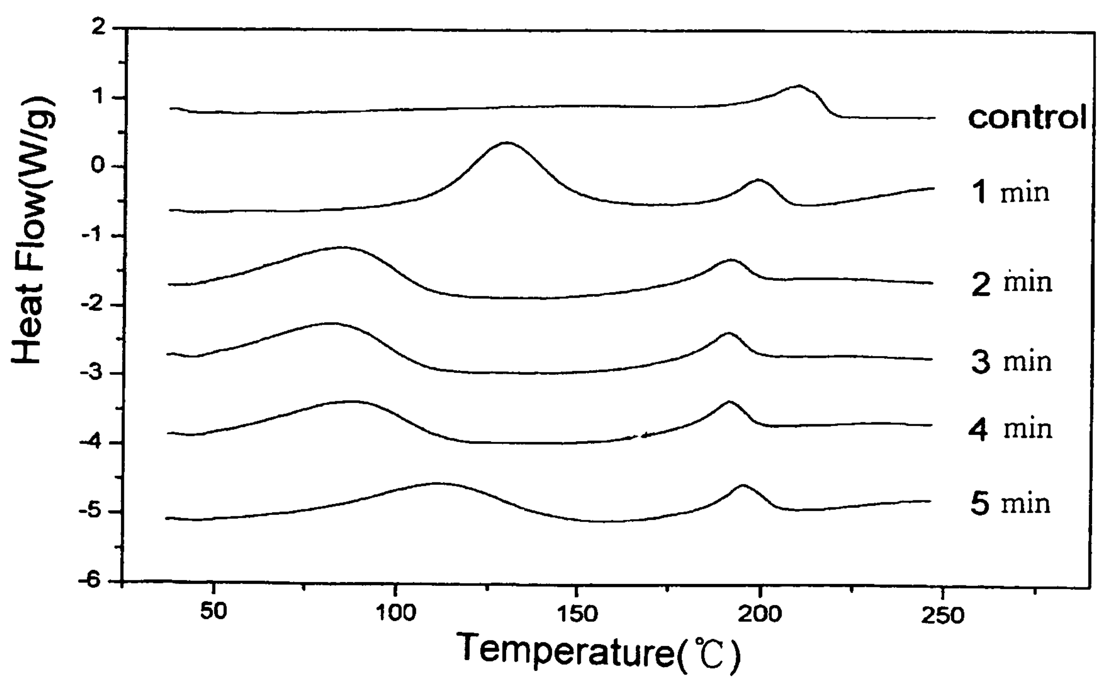

Heat Flow(W/g)
2
1
0
-1
-2
-3
-4
-5
-6
50
100
150
200
250
Temperature(℃)
control
1 min
2 min
3 min
4 min
5 min

Fig 16

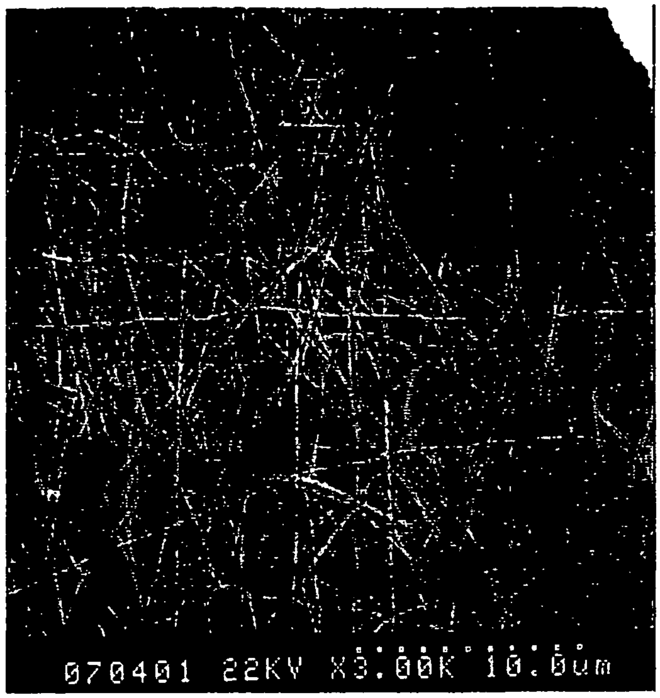


Fig 17

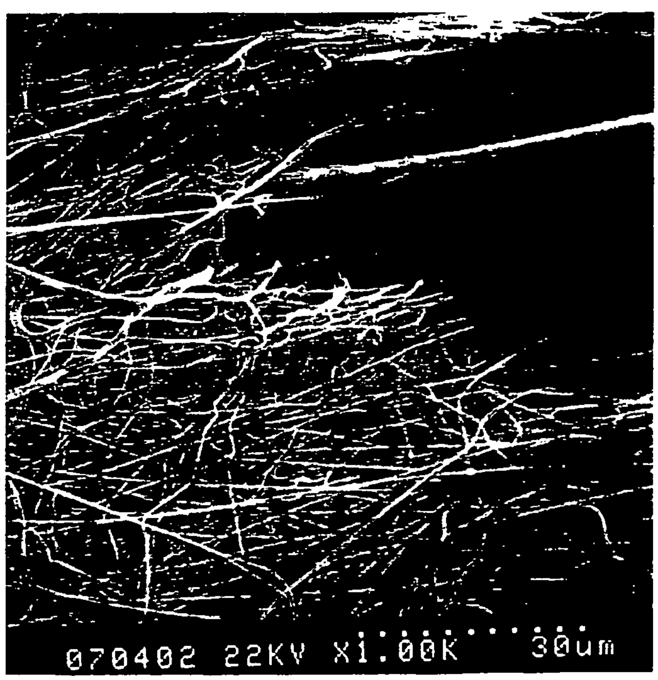


Fig 18

Fig 19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR01/02158

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 D01D 5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 D01D 5/00, D01D 5/06, D02G 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, 6106913 A (QUANTUM GROUP INC.) 22 AUGUST 2000(Family None) see the whole document	1 - 21
A	US, 6110590 A (THE UNIVERSITY OF AKRON) 29 AUGUST 2000(Family None) see the whole document	1 - 21
A	US, 5024789 A (ETHICON INC.) 18 JUNE 1991(Family None) see the whole document	1 - 21
A	US, 4965110 A (ETHICON INC.) 23 OCTOBER 1990(Family None) see the whole document	1 - 21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevence
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevence; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevence; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 APRIL 2002 (01.04.2002)	01 APRIL 2002 (01.04.2002)

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 920 Dunsan-dong, Seo-gu, Daejeon Metropolitan City 302-701, Republic of Korea	KIM, Hong Gyun
Facsimile No. 82-42-472-7140	Telephone No. 82-42-481-5616

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☑ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☑ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.